ADSORPTION OF THE METHYL ORANGE SERIES OF DYES

ON SENSITIZED SILICA GELS

by

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B.Sc.

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THE UNIVERSITY OF ALBERTA

ADSORPTION OF THE METHYL ORANGE SERIES OF DYES

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ABSTRACT

Adsorption isotherms of methyl orange and its homologs ethyl, propyl and butyl orange on specifically sensitized and control silica gels were studied.

It was found that the degree of the enhancement of adsorption and the specificity described by Dickey were erroneous. Enhancement of adsorption approximately double that of control gels was noted with some indication of specificity.

It was noted that the specificity and enhancement of adsorption could be due to surface retained dyes rather than to the lock and key mechanism suggested by Dickey.

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INTRODUCTION

A method has been reported by Dickey (1) for preparing
adsorbents having specific affinities for predetermined substances.
He prepared silica gels of a homologous series of dyes and he claims
that the gels are specific adsorbents for the sensitizing dyes. The
explanation Dickey proposes for the formation of specifically attracting
structures under these conditions is that the adsorbent in the process
of formation has accessible to it a very great number of structures
which differ only slightly in stability, and that in the presence of
a foreign molecule those structures that are stabilized through
attraction for the foreign molecule are preferentially assumed. The
adsorbent is thus pictured as automatically forming pockets that fit
closely enough to the foreign molecule to hold it by van der Waals
forces, hydrogen bonds, interionic attractions, and other types of
molecular interaction. The same mechanism has been proposed by Pauling
(2) for the formation of antibodies, with the antigen molecules serving
as a template; the latter mechanism was the theoretical basis for the
presumed manufacture of artificial antibodies reported by Pauling and
Campbell (3).

The following experimental procedure was followed by Dr. Dickey
and the results listed are from his original work (1). Experimentally,
silica gels were prepared in the presence of methyl orange and its
homologs -- ethyl, n-propyl, and n-butyl orange. These compounds have
the following structure:
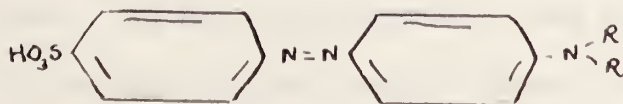
where R represents the radical named.

Then 1 gm. of adsorbent was brought into equilibrium with 10 gm. of standard dye solution, 1.5×10^{-5} molar in 5% acetic acid. The final concentration was measured spectrophotometrically and the quantity adsorbed calculated by difference.

In tabulating the results the following characteristics were defined:

"Adsorption Power": The ratio of the concentration on the gel (per gram gel) to that in the supernatant liquid (per gram liquid).

"Relative Adsorption Power": The ratio of the adsorption powers of sensitized gels to that of the adsorption power of control gels for the same dye.

Using the above definitions to calculate the results, the following were obtained:

TABLE I

| | Adsorption Power | | | |
	Methyl orange	Ethyl orange	Propyl orange	Butyl orange
Control gel	84	80	240	320
Specific adsorbent	300	740	5000	5000

TABLE II

| | Relative Adsorption Power | | | |
	Methyl orange	Ethyl orange	Propyl orange	Butyl orange
Gel prepared with:				
Methyl orange	3.5	1.6	1.1	1.1
Ethyl orange	2.5	9	2.1	2.2
Propyl orange	2.3	5	20	6
Butyl orange	1.5	2.8	5	15

There are indications of enhanced and specific adsorption in all cases. By way of explanation it was proposed by Dickey that the different alkyl groups formed different pockets into which they later adsorbed preferentially.

It may be noted that in the original work only one initial concentration was employed. This has very little significance in adsorption studies. In fact Dickey's method of calculating the adsorption is open to criticism which will be made later.

It was decided in this work to obtain complete adsorption isotherms, to compare the results with those given by Dickey, and if possible to ascertain the nature of any specificity of adsorption.

<center>EXPERIMENTAL</center>

Synthesis of Methyl Orange and Its Homologs

The procedure used was that of Slotta (4). 0.1 mole of dimethyl-, diethyl-, n-dipropyl-, and n-dibutylaniline in 120 ml. of cooled glacial acetic acid was added to 200 ml. of ice water suspension of 0.1 mole diazo sulfanilic acid with stirring until all the white crystals of diazo sulfanilic acid disappeared.

Methyl and ethyl orange separated immediately as purple crystals. Propyl and butyl orange were placed in the ice box until crystallization occurred.

In all cases the corresponding free acid was produced;
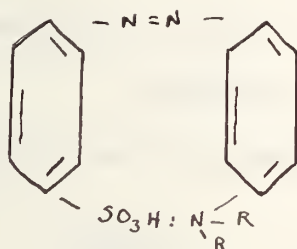
Purification of the Dyes

No general procedure has been reported in the literature for the purification of the dyes. The following procedures were employed:

Methyl and ethyl orange were brought into solution with sodium hydroxide and filtered into 6 N hydrochloric acid. The crystals were collected, washed with water and the process repeated. Finally the dyes were washed with water and oven dried at 110°C.

Propyl and butyl orange were recrystallized from diethyl ketone. The recrystallized dyes were washed with ethyl alcohol and water, then oven dried at 110°C.

Nitrogen analysis was made by a semimicro Nessler method. 98-100% purity was shown in all cases.

Absorption Spectra

The absorption of light was measured with the Beckman spectrophotometer, model DU, at approximately 25°. One-cm. corex cells were used. Molecular extinction coefficients ε were calculated from the equation

$$\varepsilon = \frac{1}{cd} \log_{10} \frac{I_0}{I}$$

where I_0 is the intensity of the light emerging from the solvent, I the intensity of light emerging from the solution, c the molar concentration of the solute, and d the thickness of the absorption cell in centimeters.

At a pH $\simeq$ 9.0 the following extinction coefficients were calculated at the corresponding maxima.

TABLE III

EXTINCTION COEFFICIENTS OF METHYL ORANGE AND ITS HOMOLOGS AT pH $\simeq$ 9.0

Anion	λ_{max} mμ	ε_{obs}	ε_{lit} (5)
methyl orange	465	26,700	26,800
ethyl orange	475	31,200	31,500
propyl orange	480	34,200	34,000
butyl orange	480	36,400	33,900

In a 5% glacial acetic acid solution, pH $\simeq$ 2.3, the following extinction coefficients were calculated at 510 mμ and used as standards.

TABLE IV

EXTINCTION COEFFICIENTS OF METHYL ORANGE AND ITS HOMOLOGS AT pH $\simeq$ 2.3

Dye	λ mμ	ε_{obs}
methyl orange	510	44,600
ethyl orange	510	20,500
propyl orange	510	37,300
butyl orange	510	42,000

Preparation of Gels

The equivalent of 30 ml. sodium silicate, Baker, (40°Be) in 275 ml. distilled water and 0.5 gm. of dye was brought to boiling,

30 ml. glacial acetic acid was added and the mixture stirred until gelation began. The gel was air-dried and ground to 48-200 mesh (Tyler Standard). The ground gel was washed well with water to remove all traces of sodium acetate. Finally the gels were extracted by methanol in a soxhlet until all possible dye was removed, then they were oven dried at 110°C.

Gel Characteristics

All gels retained colour, ranging from light pink for methyl orange sensitized gel to dark pink for butyl orange sensitized gel.

The pink colour turned to yellow upon the addition of sodium hydroxide or sodium carbonate solution, thus suggesting the change
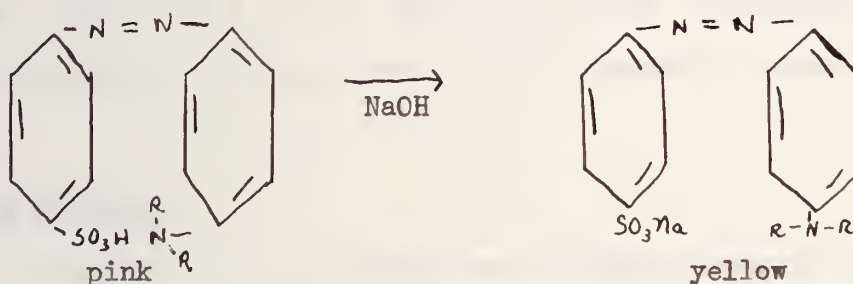
The entrained or otherwise held dye was not oxidizable by hot concentrated acidic $KMnO_4$, cold concentrated acidic $CeNH_4(SO_4)_2$ or dilute boiling nitric acid. Ordinarily, the first oxidation step with dilute nitric acid involves the formation of the azoxy compound at approximately 80°C.
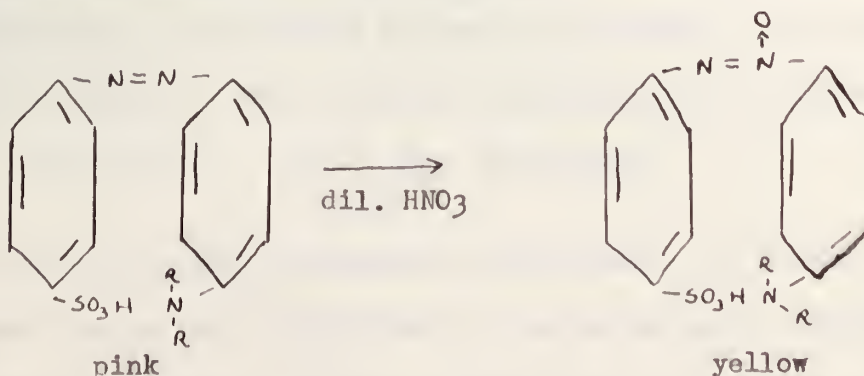
All colour was removed by heating the gels to 270°C, which is some-what above the decomposition points of the whole dye series (204° to 245°C)

Adsorption Procedure

One gram samples of dried silica gel were weighed to four significant figures in glass stoppered erlenmeyers and 100 ml. of various concentrations of the dyes in 5% glacial acetic acid added. The range chosen for the concentrations was 5.0×10^{-6} to 6.0×10^{-5} molar. Below the lower limit accuracy in reading transmission coefficients is poor; above the upper limit, colloidal and super saturated solutions occurred.

The system was allowed to attain equilibrium at 25°C for three days.

The above procedure applied to results obtained thus far. It has been found that a 2.5 gm. sample and 250 ml. of solution decreased scattering of the graphical points because of better sampling.

Desorption Procedure

Twenty-five ml. of solution was withdrawn from the equilibrated solutions, 25 ml. 5% glacial acetic acid added, and the system allowed to attain equilibrium in three days at 25°C before final readings were taken.

Analysis

The transmission coefficients of all solutions, before and after adsorption, were obtained by use of the Beckman spectrophotometer, model DU, at 510 mμ. The adsorption was calculated by difference.

$$\text{Adsorption} = \frac{\lambda_I - \lambda_F}{10 \mathcal{E} \, g} \text{ moles/gram.}$$

where λ_I is the initial transmission coefficient, λ_F is the equilibrium transmission coefficient, $\mathcal{E}$ is the molecular transmission coefficient of the dye at 510 mμ in 5% glacial acetic acid solution

(Table IV), g is the weight of the sample in grams, and the factor

10 converts from 1 litre to 100 millilitres.

$$\text{Equilibrium Concentration} \; = \; \frac{\lambda F}{\mathcal{E}} \; \text{moles/litre}$$

where the symbols are as before.

RESULTS AND DISCUSSION

The adsorption isotherms for the dyes on the various gels are shown in Figures 1 to 4. Figure 5 shows a typical adsorption-desorption isotherm.

A typical isotherm of a substance which produces a mono-layer as postulated in the dye adsorption method for the measurement of surface areas of crystals is shown below in fig. (a); whereas fig. (b) represents the typical curve obtained in this work.
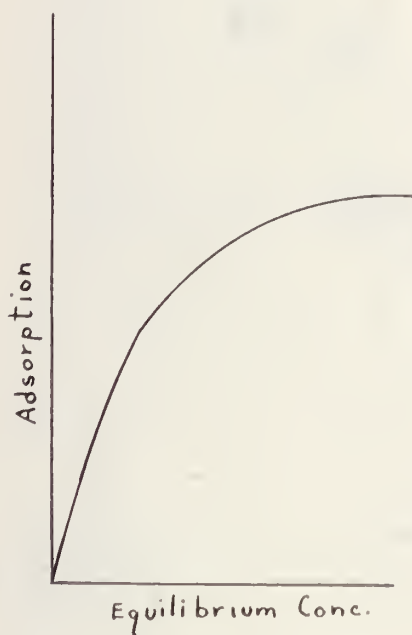
(a)   (b)
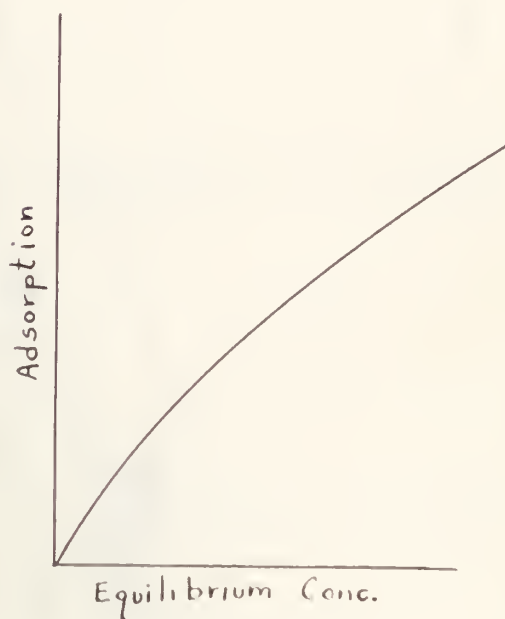
It can be seen that no maximum value is reached in fig. (b). Beyond the end of this curve supersaturated and colloidal solutions occur.

Fig. 1 Adsorption of Methyl Orange on Silica gels
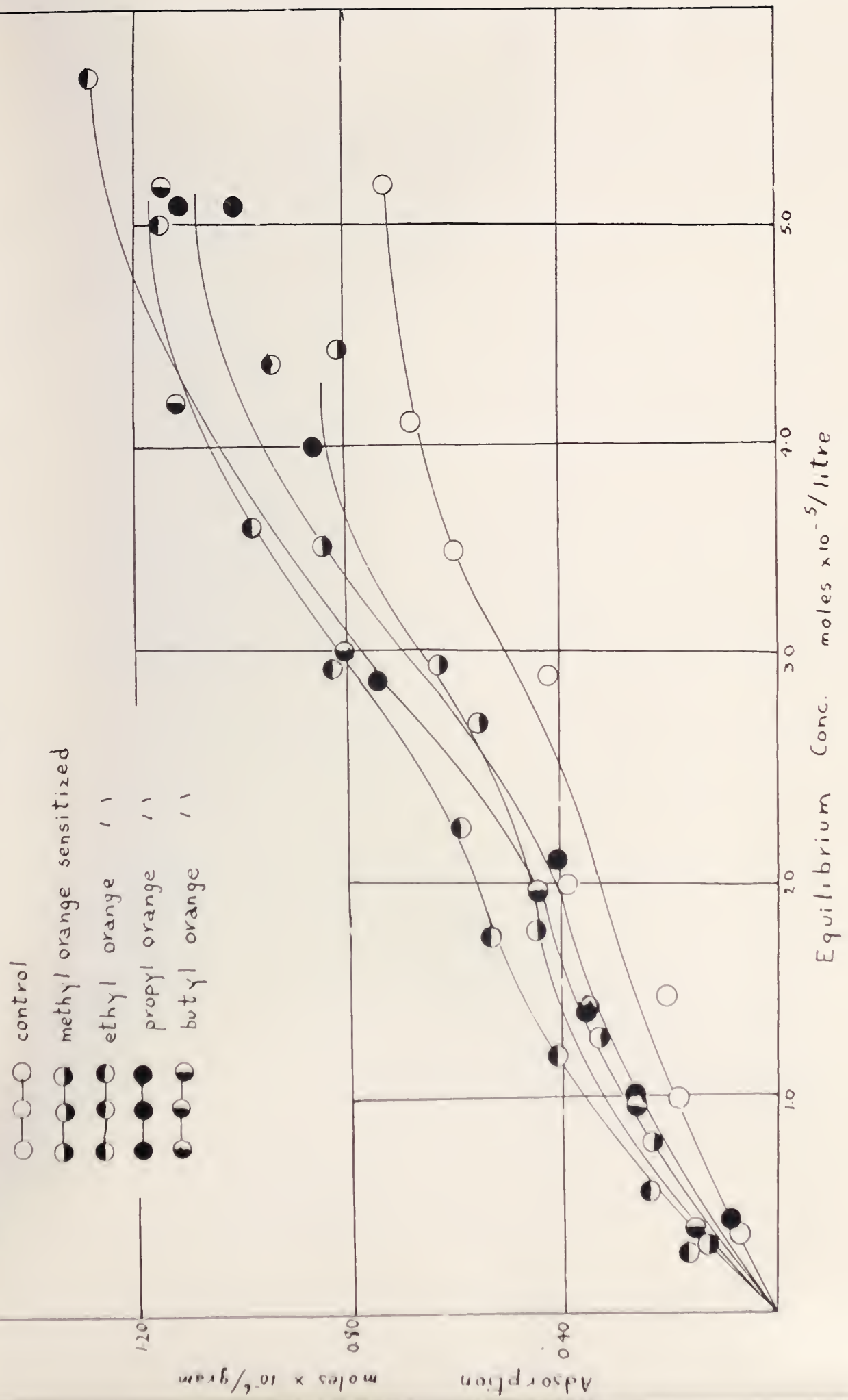
Fig. 2. Adsorption of Ethyl Orange on Silica gels
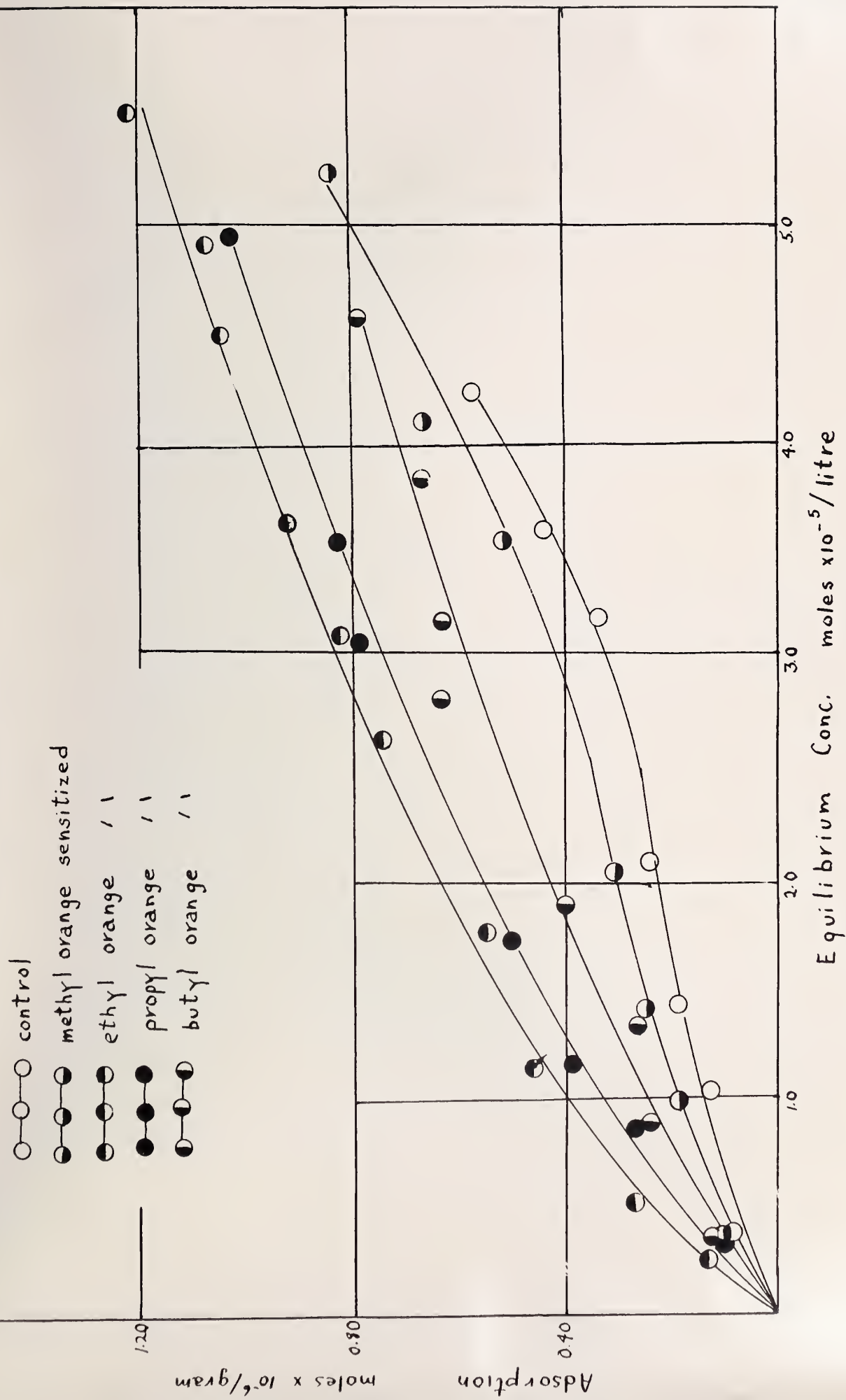
Fig 3. Adsorption of Propyl Orange on Silica gels.

control
methyl orange sensitized
ethyl orange '' ''
propyl orange '' ''
butyl orange '' ''

Adsorption moles x 10⁻⁶/gram

Equilibrium Conc. moles x10⁻⁵/litre
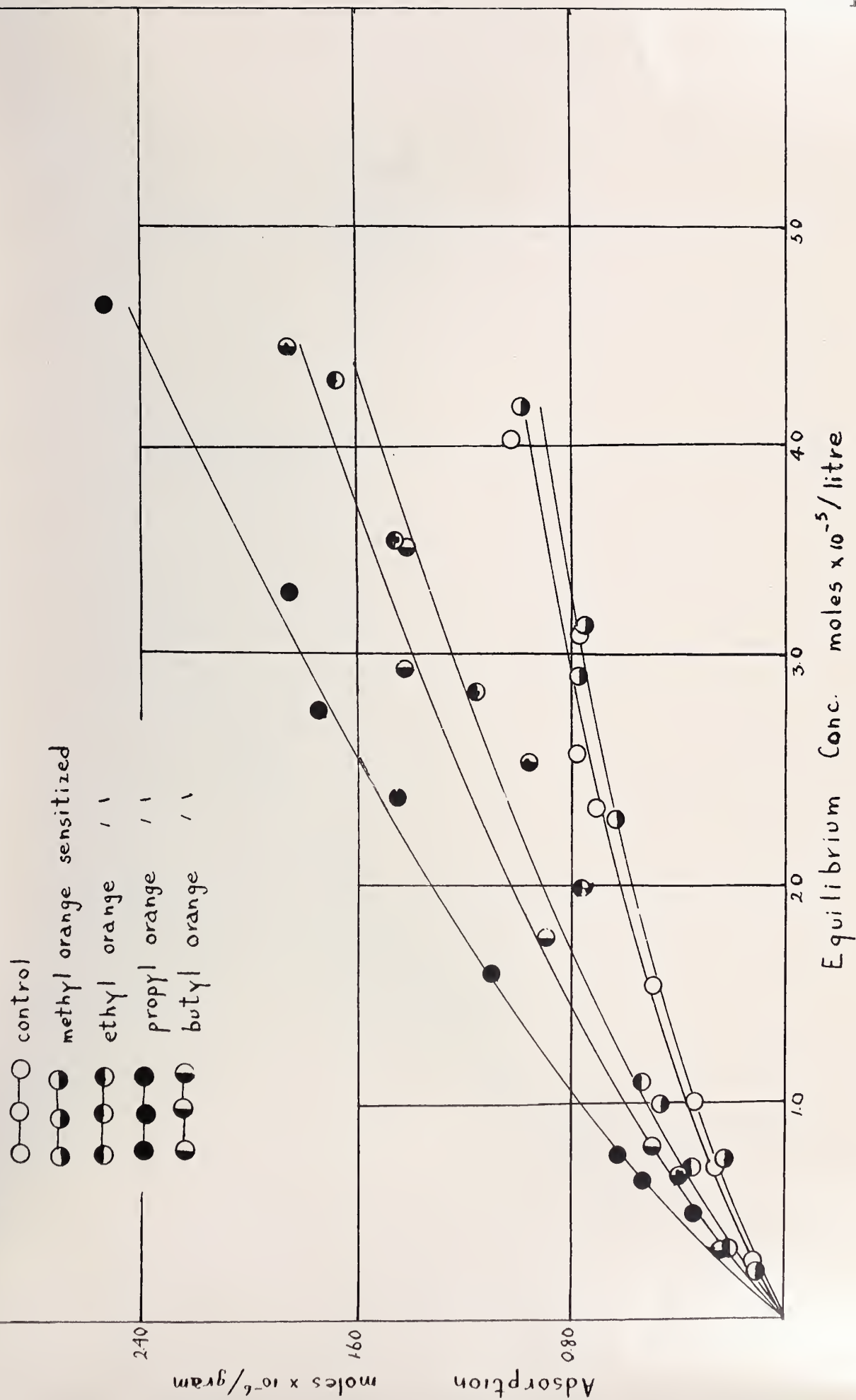
Fig. 4 Adsorption of Butyl Orange on Silica gels

control
methyl orange sensitized
ethyl orange '' ''
propyl orange '' ''
butyl orange '' ''

Adsorption moles x 10⁻⁶/gram

Equilibrium Conc. moles x10⁻⁵/litre
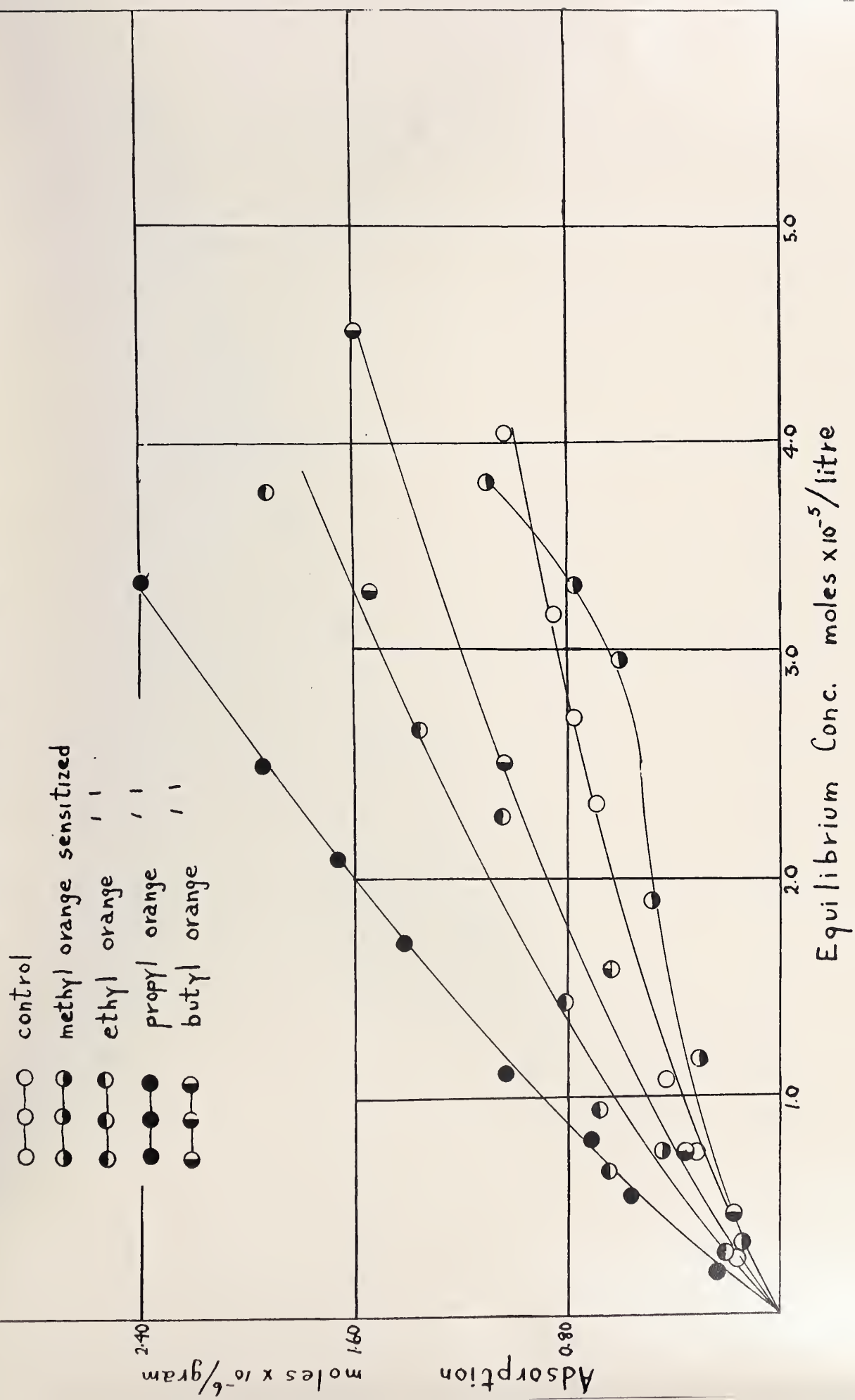
Fig. 5 Adsorption of Ethyl Orange on Ethyl Orange Sensitized Gel.

Adsorption ● Desorption ○

Adsorption moles x 10^{-6}/gram

Equilibrium Conc. moles x 10^{-5}/litre
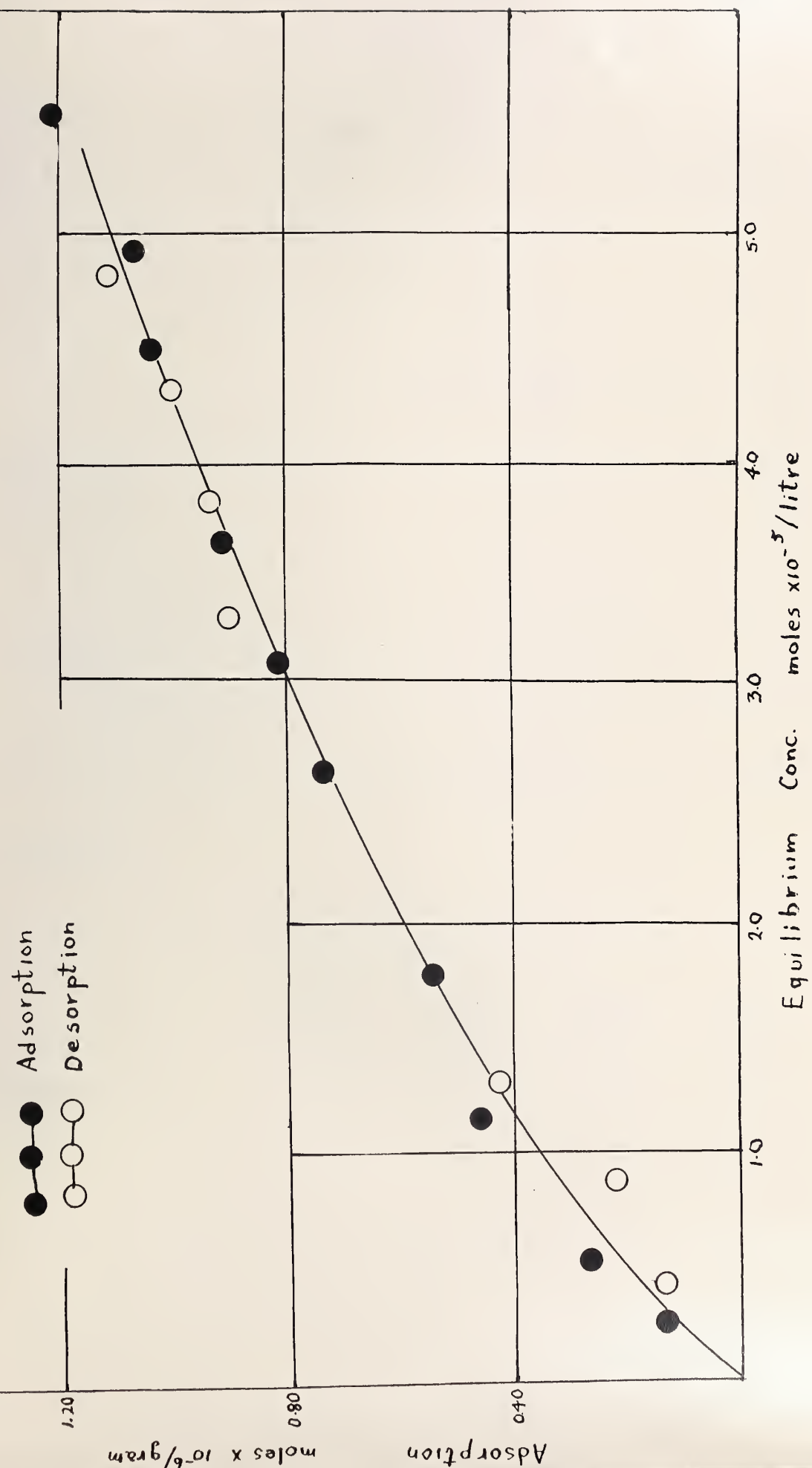
To compare the data obtained with that of Dickey, adsorptions at a constant equilibrium concentration are tabulated in Tables V, VI, and VII. The equilibrium concentration chosen is somewhat arbitrary, namely 1.5×10^{-5} M, but it lies in the region of least probable error.

TABLE V

ADSORPTION OF DYES ON SILICA GELS (moles x 10^{-6}/g.)

| Dye | Gel | | | | |
---	Control	Methyl orange	Ethyl orange	Propyl orange	Butyl orange
Methyl orange	0.25	0.40	0.50	0.37	0.34
Ethyl orange	0.19	0.25	0.51	0.43	0.35
Propyl orange	0.48	0.44	0.62	1.08	0.78
Butyl orange	0.50	0.42	0.92	1.28	0.72

Adsorption power is defined here as the amount of dye / g. of gel adsorbed at 1.5×10^{-5} M equilibrium concentration.

Relative adsorption power is the ratio of adsorptions for sansitized and control gels at this concentration.

These definitions differ fundamentally from those of Dickey (Appendix B).

TABLE VI

ADSORPTION POWER (moles x 10^{-6}/g.)

	Methyl orange	Ethyl orange	Propyl orange	Butyl orange
Control	0.25	0.19	0.48	0.50
Specific Adsorbent	0.40	0.51	1.08	0.72

TABLE VII

RELATIVE ADSORPTION POWER

| Dye | Gel | | | |
	Methyl orange	Ethyl orange	Propyl orange	Ethyl orange
Methyl orange	1.60	2.00	1.48	1.36
Ethyl orange	1.32	2.68	2.26	1.85
Propyl orange	0.92	1.29	2.25	1.63
Butyl orange	0.84	1.84	2.56	1.44

It is obvious that there is a large discrepancy between the results obtained here and those obtained by Dickey. This may be seen by comparing Table VI to Table I and Table VII to Table II. In no case does over a hundred-fold increase in adsorption power, or a twenty-fold increase in relative adsorption power occur. These very large increases are only apparent as will be explained in Appendix B.

In general it can be stated that an enhancement of $1\frac{1}{2}$ to 2 times the adsorption of the control gels occurs by the sensitizing process. Also the specificity is so low that it can be masked by gel fluctuations. For example two control gels differ by as much as 25% and two gels prepared with the same dye may differ by as much as 50%.

Since the high specificity reported by Dickey does not exist (Appendix B), the theoretical considerations advanced by him are questionable. Under the section "Gel Characteristics", it was stated that all sensitized gels retained colour, the dye apparently being bound on the surface with very tight bonds. The surface characteristics of a silica gel would be changed by these retained molecules, with a change of adsorption likely to be that of the order obtained. The factors that would have an effect on adsorption are:

the basicity of the dyes, the saturation concentration as a measure of the chemical potential of the individual dyes, and the particular dye retained on the surface. It is probable that the latter factor gives rise to whatever specificity there is because of the known tendency for these dyes to polymerize. The variability, which is higher for sensitized than for control gels, would then be explained by a variation in the amount of dye retained during the preparation of the gel.

It can be added in support of the latter hypothesis that gels made in the presence of sulfanilic acid and p-p' diamino diphenyl enhance adsorption $1\frac{1}{2}$ to 2 times that of the control gel. This fact does not support the hypothesis advanced by Dickey since the gels would not have pockets remotely resembling the molecular shape of the dyes used.

However, both these substances are bi-functional (as are the dyes used) and while held to the surface of the gel, they may serve as centres of attraction for the adsorbate molecules. This supports the present hypothesis.

Suggestions

Further work could be carried out to test the gel characteristics after removal of the tightly-bound dye. This dye may be removed by either of the two following ways.

(a) Oxidation with hot concentrated sulfuric acid and $CeNH_4(SO_4)_2$.

(b) Heating in a furnace to 300°C.

Controls would have to be made using the same method, two different controls and specific adsorbents being run to check whether the percentage change in adsorption is consistent.

It is hoped that the above experiment will give a clear cut distinction between a process as described by Dickey and that presented in the present discussion.

Also, work could be carried out to ascertain the effects of pH upon adsorption. Care must be taken that the buffering solution will have no electrolyte effect upon the gel (10).

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Discussion of Methyl Orange and Its Homologs

Much controversy exists over the structure and nature of
methyl orange and its homologs. Different melting points and decom-
position points are reported by various workers. It has even been
postulated by Karrer (6) that mono n-butyl orange is produced in the
coupling process rather than di n-butyl orange. This has been refuted
by the work of Slotta and Franke (4), and the present work leads to
an agreement with the latter authors.

In view of the discrepancies that exist in the literature
it was decided to prepare the series by an independent method and to
compare the extinction coefficients of the new series to those obtained
previously. It is evident that difficulties may arise in one or
more of the following processes, (a) diazotization, (b) coupling, (c)
purification. With a controlled reaction rate a product of good
composition might be obtained. To control the first step slightly
soluble silver nitrite was used, for it had the advantage of tying
up the diazo sulfanilic acid as a slightly soluble silver salt. This
factor controlled the coupling process, which proceeded so slowly
that sodium chloride had to be added to precipitate the silver ion.
Excess of the di-aniline was added to form the salt.

This compound had the added advantage of being readily recrystallized

from water.

Using di-methyl aniline as an example the following procedure was
followed:

Silver nitrite and a slight excess of sulfanilic acid were
added to an ice water mixture and stirred until the reaction was
completed. Over a mole excess of di-methyl aniline was added and the
solution stirred. A cold sodium chloride solution was added slowly
with stirring until all silver was precipitated as the chloride. The
golden yellow crystals were collected at the pump, then brought into
solution with hot water, filtered, and cooled until crystallization
took place. The crystals were collected at the pump and the process
repeated.

The di-methyl aniline salt was converted to the free acid
by heating in an acetic acid - acetone solution. The crystals were
collected at the pump, washed first with 6 N hydrochloric acid, then
with distilled water.

As yet no constants have been obtained for this new series.
The golden yellow flakes (m.p. 115°C) previously reported as methyl
orange (7) are in reality the di-methyl aniline salt of methyl orange.

The melting point (115°C) is in reality a decomposition point for the
reaction:
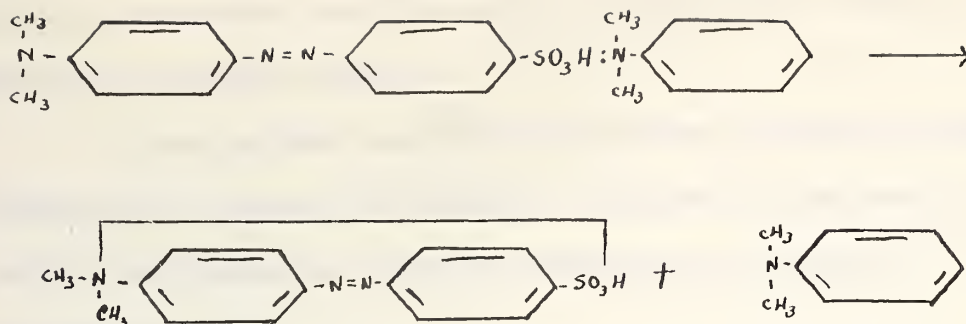
As much controversy exists over the nature of the dye
solutions as for the synthesis of the dye series. Methyl orange and
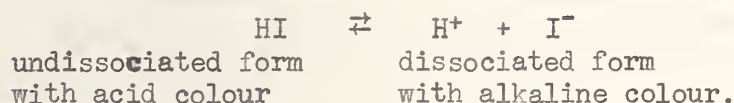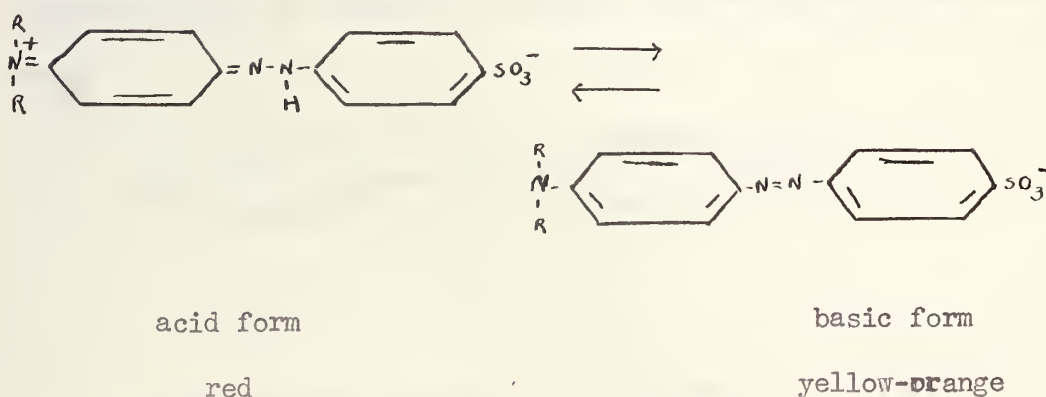its homologs are classified as acid indicators. Under the simple
indicator theory (8) these may exist in an undissociated form and a
dissociated form and according to the definition the following equili-
brium exists

$$HI \rightleftarrows H^+ + I^-$$

undissociated form   dissociated form
with acid colour   with alkaline colour.

For methyl orange and its homologs the following structures have
been postulated (9).

acid form   basic form

red   yellow-orange

Using this postulate it is difficult to understand the large
difference of solubility obtained between the two forms. The present
experimental work points to a solubility of approximately 1×10^{-4}
moles/litre for the series for the acid form, whereas the basic forms
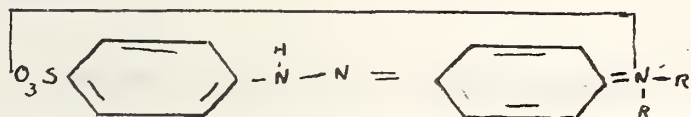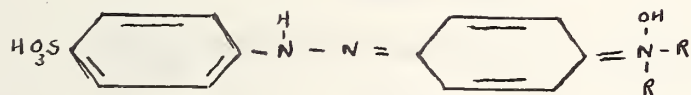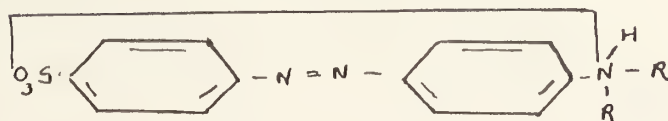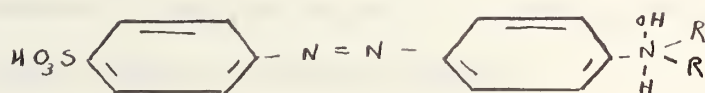have solubilities up to 0.5 moles/litre. The above postulated forms

lead to a conclusion that the acid form should be as soluble (if not more so) as the basic form.

Other authors have devised more than two forms for methyl orange and its homologs in solution. Prideaux (9) has the following listed, considering the series as amphoteric in character.

Red quinoid forms:

$$HO_3S - \langle \rangle - \overset{H}{\underset{}{N}} - N = \langle \rangle = \overset{OH}{\underset{R}{N}} - R$$

$$^-O_3S - \langle \rangle - \overset{H}{\underset{}{N}} - N = \langle \rangle = \overset{+}{\underset{R}{N}} - R$$

The inner salt is changed partially when dissolved in water, and then completely upon the addition of alkali into the salts of the azoid forms:

$$HO_3S - \langle \rangle - N = N - \langle \rangle - \overset{OH}{\underset{H}{N}} \overset{R}{\underset{R}{<}}$$

$$^-O_3S - \langle \rangle - N = N - \langle \rangle - \overset{H}{\underset{R}{N}} - R$$

Due to such diverse opinion it is difficult to envisage the solution equilibria and to arrive at a conclusion as to which form

is adsorbed. Furthermore, if only one form is adsorbed, then concentration is not a reliable estimate of chemical potential of the adsorbate.

It was stated that the relative adsorption is dependent upon the relative basicity of the dye series. The $K_{ind.}$ may serve as a standard of comparison. The following values were published by Slotta and Franke (4).

TABLE VIII

$K_{ind.}$ OF METHYL ORANGE AND ITS HOMOLOGS

| Dye	$K_{ind.}$ (pH)	Range (pH)
Methyl orange	3.76	3.1 - 4.4
Ethyl orange	4.39	3.1 - 4.6
Propyl orange	3.95	3.2 - 4.3
Butyl orange	4.01	3.4 - 4.7

The pH's chosen for the determination of the extinction coefficients (Table III and Table IV) lie well outside the above range. At a pH of 9.0 there is present 100% azoid form, at a pH of 2.3 there is present approximately 100% quinoid form. This makes it difficult to explain the extremely low extinction coefficient of ethyl orange in acidic solution and the shift in positions of propyl and butyl oranges. These may be due to impurities but most likely are due to some inherent structural change.

APPENDIX B

A Criticism of Dickey's Work

All of Dickey's adsorption measurements (1) were made by equilibrating 1 g. of gel with 10 g. of dye solutions of the same initial concentration. Let us consider two hypothetical gels A and B which differ in adsorptive capacities. Let x be the initial concentration of dye in moles per gram of solution, and let a and b be the respective amounts of dye adsorbed per gram of gel, such that a > b. The following situation will take place:
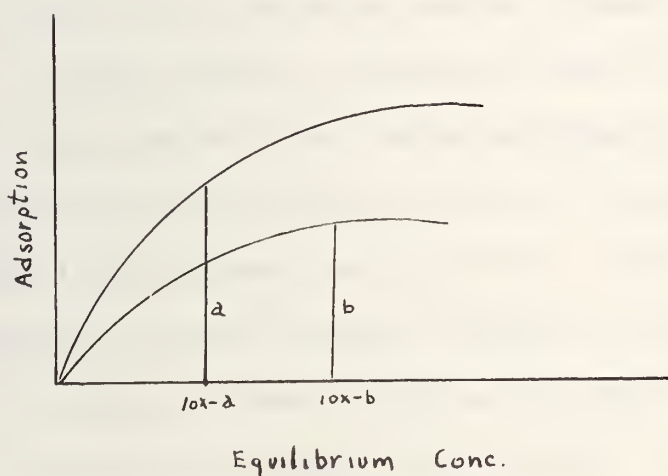
Equilibrium Conc.

The curves represent the adsorption isotherms of the dye on gels A and B.

It can be seen that the comparison of adsorptions will be made at different equilibrium concentrations (10x - a) and (10x - b). Furthermore the definition of adsorption power $\dfrac{a}{10x - a}$, $\dfrac{b}{10x - b}$ leads to an enhancement of results in favour of the gel A at any concentration since 10x - a < 10x - b. This effect is even more magnified since the equilibrium concentrations achieved in the original work

are so low that a slight variation would magnify the results tremendously.

It is due to this magnification that Dickey arrived at the conclusion that there is a large enhancement of adsorption with high specificity. A comparison of adsorptions at the same equilibrium concentration (b to b + c) does not lead to such results, as has been shown in this work.

Secondary considerations which do not appear in the original work and which could produce large errors are the following:

pH change

It was found that extraction of the dye with methyl alcohol does not remove all of the sodium acetate produced in the original reaction. Besides causing a considerable error in the weighing of the gel, sodium acetate forms a buffer solution with acetic acid. The original dye solution had a pH of 2.3. The equilibrium solution with sodium acetate present had a pH of 4.0. All of the dyes used are indicators and shift from red to yellow in a more basic solution. Since all readings were made at 510 mμ this would produce a large error. To correct this situation the gels were thoroughly washed with water.

Concentration

The initial concentration employed by Dickey was such that the equilibrium concentration attained was so low that there was a large probable error in reading the transmission coefficient on the Beckman spectrophotometer. It was found that a 1 g. sample of the gel was not homogeneous enough to produce constant values. Further, the use of such low initial concentrations with his method of calculation would lead to results which could vary a large amount from the true value.